APPENDIX E TO PART 50 [RESERVED]

APPENDIX F TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

PRINCIPLE AND APPLICABILITY

1. Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). (*1,2,3*) NO_2 is first quantitatively reduced to NO(*4,5,6*) by means of a converter. NO, which commonly exists in ambient air together with NO_2, passes through the converter unchanged causing a resultant total NO_X concentration equal to NO+NO_2. A sample of the input air is also measured without having passed through the converted. This latter NO measurement is subtracted from the former measurement (NO+NO_2) to yield the final NO_2 measurement. The NO and NO+NO_2 measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

2. *Sampling considerations*.

2.1 Chemiluminescence NO/NO_X/NO_2 analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (*7*) Atmospheric concentrations of these potential interferences are generally low relative to NO_2 and valid NO_2 measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known or suspected to be high relative to NO_2, the use of an equivalent method for the measurement of NO_2 is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence NO/NO_X/NO_2 analyzers is optional and left to couraged. The sample residence time between the sampling point and the analyzer should be kept to a minimum to avoid erroneous NO_2 measurements resulting from the reaction of ambient levels of NO and O_3 in the sampling system.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence NO/NO_X/NO_2 analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO_2 measurements and therefore filters should be changed frequently.

3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

CALIBRATION

1. *Alternative A*—Gas phase titration (GPT) of an NO standard with O_3.

Major equipment required: Stable O_3 generator. Chemiluminescence NO/NO_X/NO_2 analyzer with strip chart recorder(s). NO concentration standard.

1.1 *Principle*. This calibration technique is based upon the rapid gas phase reaction between NO and O_3 to produce stoichiometric quantities of NO_2 in accordance with the following equation: (*8*)

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO/NO_X/NO_2 analyzer is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 from a stable uncalibrated O_3 generator. (*9*)

1.2 *Apparatus*. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be of glass, Teflon®, or other non-reactive material.

1.2.1 *Air flow controllers*. Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 *NO flow controller*. A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive material.

1.2.3 *Air flowmeters*. Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

1.2.4 *NO flowmeter*. A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 *Pressure regulator for standard NO cylinder*. This regulator must have a nonreactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 *Ozone generator*. The generator must be capable of generating sufficient and stable levels of O_3 for reaction with NO to generate